Grafting of Living Polystyrene onto Poly(methyl methacrylate) and Its Copolymer (Commemoration Issue Dedicated to Professor Hiroshi Ibagaki, Professor Michio Kurata, Professor Ryozo Kitamura, On the Occasion of Their Retirments)

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Grafting of Living Polystyrene onto Poly(methyl methacrylate) and Its Copolymer*

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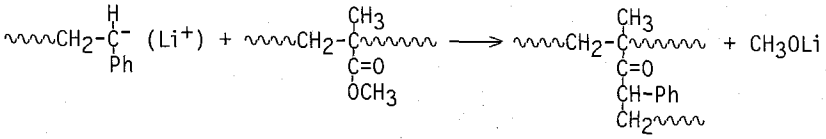
Grafting of anionic living polystyrene (PS) onto poly (methyl methacrylate) (PMMA) and MMA copolymer was examined. This reaction was found to be a nonrandom process, namely grafting at the MMA units adjacent to the already grafted unit is hard to occur for steric reasons. It was also found that the grafting reaction is accompanied by side reactions leading to the scission of the main chains and the dimerization of the precursor PS chains. Possible mechanisms of the scission and dimerization were suggested.

KEY WORDS: Nonradom grafting/ Steric hindrance/ Chain scission/ Dimerization of precusor side chains

INTRODUCTION

Garfting of anionic living polystyrene (PS) onto poly(methyl methacrylate (PMMA) have attracted considerable attention[1-3] as one of the simplest routes to new materials which are grouped among polymer alloys. In this gafting reaction, the PS anion is believed to attack the ester group of the MMA unit to form a graft copolymer as shown in the following scheme:



It has been known that a similar reaction occurrs as a side reaction in the stepwise block copolymerization of styrene S and MMA, when MMA, the second monomer, is introduced into the solution of the living PS[4,5].

We have examined this grafting reaction in detail to find that it is accompanied by some unexpected side reactions including the scission of the backbone (PMMA) chains and the dimerization of the PS precursors. Details of the side reactions will be given below.

EXPERIMENTAL

Materials. Styrene and benzene were purified according to the standard methods employed for anionic living polymerization in vacuo[5]. Four living PS's in benzene

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solution each in a flask with a breakable seal were prepared by using n-butyllithium as initiator. Two anionically prepared PMMA's[6] and one S-MMA alternating copolymer[7] (coded as SMAL) prepared by using ethylaluminium sesquichloride as catalyst were employed as backbone polymers. The molecular characteristics of the polymers are given in Table I.

Table I. Molecular Charcteristics of Backbone and Grafting Chains.

Mol. Wt.	Backbone Chain			Grafting Chain			
	PMMA-1	PMMA-2	SMAL[a)]	PS-1	PS-2	PS-3	PS-4
$10^{-4}M_n$	44.5	91.6	44.9	2.89	0.57	1.17	1.27
$10^{-4}M_w$	62.8	110.0	64.2	3.44	0.83	1.34	1.46

[a)] Styrene-methyl methacrylate alternating copolymer.

Grafting Reactions. A known amount of a backbone polymer (PMMA or SMAL) was dissolved in purified benzene in vacuo. A small amount of diphenylethyllithium, which was confirmed to purify the system without any unfavorable reaction with the polymer, was added to the system. The solution was mixed with the living PS solution at 25°C with vigorous stirring. In all cases, the concentration of MMA units was nearly the same, i.e., about 2×10^{-4} M. The reaction was terminated by a few drops of methanol. The polymer product was recovered as a precipitate in a large excess of methanol.

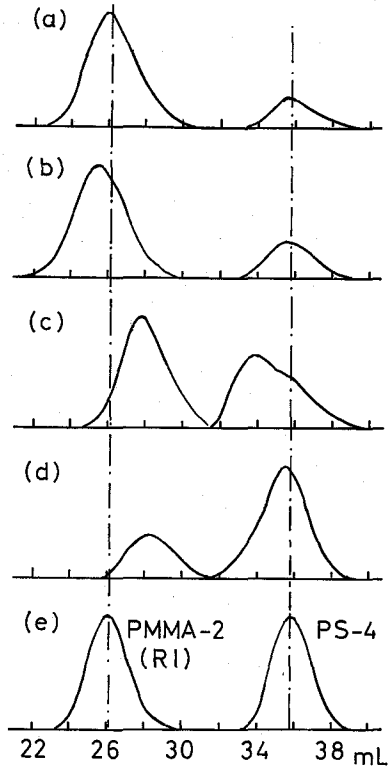

Fig. 1. UV-detected GPC chromatograms for series-4 samples (a-d) and the precursor polymers (e): PMMA, the backbone polymer, as being transparent for UV, was detected by means of RI (refractive index).

Gel Permeation Chromatography (GPC). The extent of grafting of the PS living ends was evaluated on the basis of the GPC chromatogram taken by the use of a UV detector. Excepting a few cases, the precursor (ungrafted) PS and the graft copolymer gave elution curves well separated from each other, as Figure 1 shows. Since PMMA shows no absorbance for UV, the ratios of the areas below the two curves may be identified with the ratio of the grafted and ungrafted PS's. The chromatogram for the ungrafted PS was sometimes skewed because of the third component overlapping on it. Even in such a case, we regarded the total (skewed) chromatogram as due to the precursor PS for the reson described later.

Light Scattering. Each reaction product in benzene solution was studied by light scattering for the weight-average molecular weight M_w. Experiments were made at 30°C on a Fica light scattering photometer Model 50 by using a vertically polarized light of 436 nm. The molecular weight $M_{w,cop}$ of the graft copolymer component was evaluated according to the following relation.

Table II. Experimental Conditions and Extents of Grafting (25°C).

Sample	Backbone chain	Grafting chain	Y[a]	Reaction time, t	R_{PS}[b] (%)	R_M[c] (%)
1 -1	PMMA-1	PS-1	0.075	3w	87.4	6.6
1 -2	PMMA-1	PS-1	0.144	3w	90.1	13.0
1 -3	PMMA-1	PS-1	0.320	3w	75.7	24.2
1 -4	PMMA-1	PS-1	0.690	3w	24.8	17.1
21-1	PMMA-2	PS-2	0.057	10m	90.5	5.2
21-2	PMMA-2	PS-2	0.124	10m	90.4	11.2
21-3	PMMA-2	PS-2	0.280	10m	87.9	24.6
21-4	PMMA-2	PS-2	0.524	10m	74.5	39.0
22-1	PMMA-2	PS-2	0.280	1h	87.5	24.5
22-2	PMMA-2	PS-2	0.280	10h	89.7	25.1
22-3	PMMA-2	PS-2	0.280	1w	86.6	24.2
23-1	PMMA-2	PS-2	0.524	1h	74.9	39.2
23-2	PMMA-2	PS-2	0.524	10h	82.3	43.1
23-3	PMMA-2	PS-2	0.524	1w	80.0	41.9
3 -1	SMAL	PS-3	0.281	10m	86.2	24.2
3 -2	SMAL	PS-3	0.605	10m	86.0	52.0
3 -3	SMAL	PS-3	0.916	10m	78.0	71.5
3 -4	SMAL	PS-3	1.460	10m	59.4	86.9
4 -1	PMMA-2	PS-4	0.226	10m	80.4	18.2
4 -2	PMMA-2	PS-4	0.596	10m	79.1	47.1
4 -3	PMMA-2	PS-4	0.808	10m	57.6	46.6
4 -4	PMMA-2	PS-4	1.170	10m	39.0	45.6

[a] Mole ratio of living PS to MMA units, [LPS]/[MMA], with [MMA] being about 2×10^{-4} mol/L in all cases.
[b] Fraction of grafted PS relative to total PS.
[c] Fraction of the MMA units having a PS graft, estimated by $R_M = YR_{PS}$.

$$M_w = w M_{w,cop} + (1-w) M_{w,PS} \quad (1)$$

where the subscript PS refers to the precursor PS, and w is the weight fraction of the copolymer coponent, as evaluated by the above-mentioned GPC analysis.

RESULTS AND DISCUSSION

Extents of Reaction

The extent of reaction R_M of the ester groups, i.e., the number fraction of the MMA units carrying a PS graft is given by

$$R_M = R_{PS} Y \quad (2)$$

where R_{PS} is the fraction of the grafted PS relative to the total PS, and Y is the mole concentration of the PS living ends relative to that of the MMA units:

$$Y = [LPS]/[MMA] \quad (3)$$

Figure 2 shows the plot of R_M versus reaction time t for two different values of Y. In each case, R_M is independent of t in the examined range of t, even though the orange color characteristic of living PS did not vanish throughout. This means that the reaction has virtually completed within the shortest t studied, i.e., 10 min.

Figure 3 shows the dependence of R_M on Y. In all cases, t is longer that 10 min, so that these data may be regarded as ultimate. The figure shows that when PMMA is a backbone polymer, R_M increases proportionally to increasing Y for Y smaller than about 0.6, but for larger Y, it levels off to a constant value of about 45%. This seems to suggest that once an MMA unit has been grafted, its two neighboring units are difficult to be grafted for steric or other reasons. Notably, a maximum R_M of 43.3% is expected by the model in which grafting is assumed to ocuur randomly allowing no adjacent

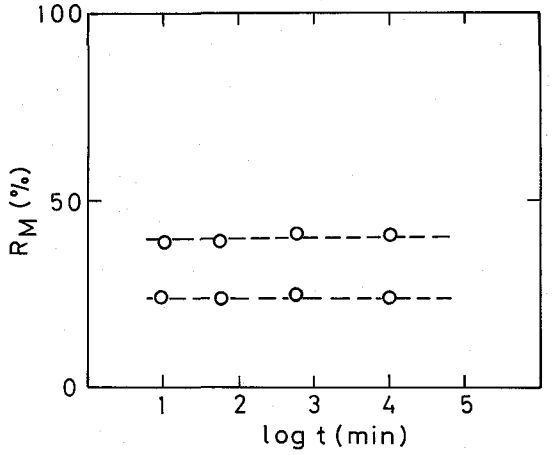

Fig. 2. Plot of R_M vs. log t for samples 21-4 (Y=0.524, upper curve) and 21-3 (Y=0.280, lower curve).

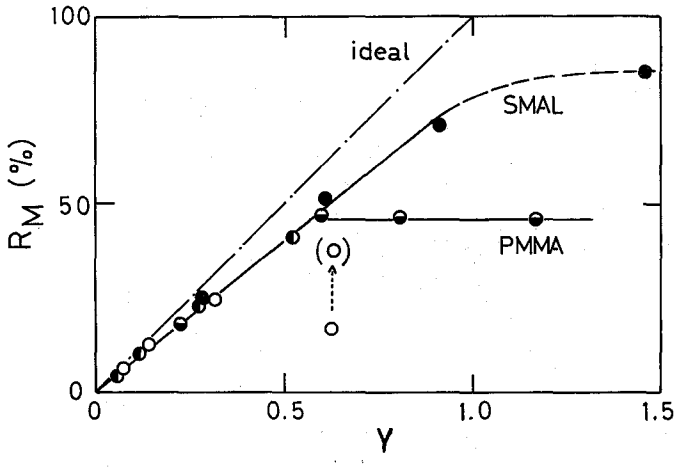

Fig. 3. Plot of R_M vs. Y for samples of series 1 (open circles), series 21 (verticlally half-filled), series 3 (filled), and siries 4 (horizontally half-filled). The circle in ( ) denotes the corrected value (see text). The chain-dot line denotes the ideal system in which $R_M=100Y$ (for $Y\leqq 1$) and $R_M=100$ (for $Y>1$).

grafting[8]. Another strong support for this model comes from the experimental results for the alternating copolymer. When SMAL is a backbone polymer, R_M reaches nearly as large as 90% for large Y (Figure 3), showing that grafting at two MMA units becomes practically independent when they are separated by one (or more) ungrafted unit(s). Interestingly, Takaki et al.[9] have reported that in the frafting of anionic living PS onto chloromethylated PS (CMPS), the maximum extent of reaction of chloromethyl units is about 80%. This value is somewhat smaller than our R_M for SMAL but definitely larger than that for PMMA. This is presumably due to the longer distance from the main chain to the reaction cites, hence less steric hindrance, in CMPS than in PMMA.

Main-Chain Scission

Anomalies were noted in the GPC patterns of the reaction products. Figure 1 shows the UV-detected chromatograms of several samples, whose preparation conditions differ only in Y. Two points should be noted in the figure. One concerns the elution peak for the copolymer component. When Y is small, the peak shifts towards the higher-molecular weight (lower-elution volume) side of the precursor PMMA peak, as one would expect (Figures 1a and b). However, when Y is relatively large, the copolymer peak shifts towards the lower-molecular weight side (Figures 1c and d). Another point concerns the elution curve corresponding to the unreacted PS component. When Y is relatively large, the curve becomes somewhat skewed with the peak position shifting towards the higher-molecular weight side of the precursor PS (Figuers 1c and d). In this section we examine the former problem, leaving the latter problem for later discussion.

The anomalous behavior of the copolymer components as observed by GPC may be most easily understood in terms of main-chain scission. Light scattering results

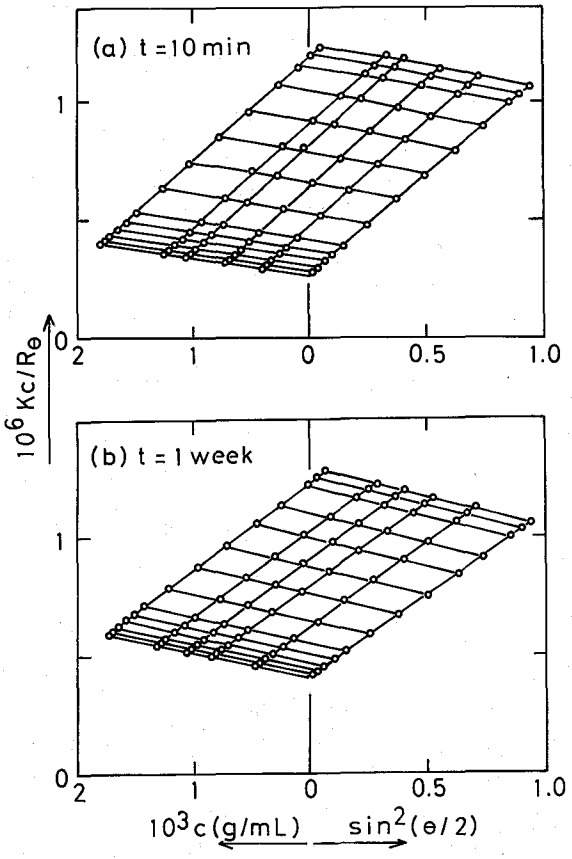

Fig. 4. Zimm plots for samples 21–3 (a) and 22–3 (b).

directly confirm this: Figure 4 shws the Zimm plots for two samples, which were prepared under the same conditions excepting reaction time t. Since they have the same values of R_M (see Table 1), their molecular weight should be the same without main-chain scission. As is evidenced by the difference in the ordinate intercepts of the Zimm plots, the M_w of the sample with $t=1$ week is markedly smaller that than with $t=10$ min. Moreover, the latter value itself is significantly smaller than is expected from the value of R_M. It is thus clear that main-chain scission is the cause for the GPC anomaly.

If a linear polymer, whose number- and weight-average molecular weights are M_n° and M_w°, respectively, and whose molecular weight distribution is of the Schulz-Zimm type[10], experiences x random scissions, its weight-average molecular weight reduces to[11]

$$M_w=(2M_n^\circ/x)\{1-(1/x)[1+(x/h)^{-h}]\} \tag{4}$$

$$1/h=(M_w^\circ/M_n^\circ)-1 \tag{5}$$

Here M_n°, i.e., the M_n of the undamaged graft copolymer, may be estimated by

$$M_n^\circ = M_{n,\,bb} + M_{n,\,PS}[a'/(1-a')] \tag{6}$$

where $M_{n,bb}$ and $M_{n,\,PS}$ are the number-average molecular weights of the precursor backbone and PS chains, respectively, and a' is the weight fraction of the PS component in the copolymer. The polydispersity index h of the undamaged copolymer may be approximated by that of the original backbone polymer with little error, especially when R_M is large. Applying the light scattering M_w values to Eq. (6), we can thus estimate the number of scission x. Results are given in Table III.

If we let DP_{MMA} be the average number of MMA units per original backbone melecule, the ratio x'

$$x' = x/DP_{MMA} \tag{7}$$

Table III. Number of Scission x and Probability of Scission x' per Ester Group.

Sample	a'[a]	$M_{n,cop}^{\circ}$[b] $\times 10^{-6}$	$M_{w,cop}$ $\times 10^{-6}$	x	$10^3 x'$	x'/Y
1 -1	0.95	8.9	4.46	2.8	0.63	8.3
1 -2	0.97	17.1	6.51	4.1	0.92	6.4
1 -3	0.99	31.8	2.44	25.0	5.6	17.6
1 -4	0.98	22.2	0.96	45.2	10.2	14.8
21-2	0.87	3.3	2.82	1.0	0.23	1.9
21-3	0.93	6.7	4.47	1.8	0.39	1.4
21-4	0.96	10.4	4.47	3.2	0.72	1.4
22-1	0.93	6.7	3.78	2.3	0.53	1.9
22-2	0.94	6.9	3.36	2.9	0.65	2.3
22-3	0.93	6.6	2.86	3.5	0.78	2.8
23-1	0.96	10.4	4.19	3.8	0.85	1.6
23-2	0.96	11.4	3.23	5.9	1.33	2.5
23-3	0.96	11.1	2.76	6.9	1.56	3.0
3 -1	0.93	6.8	7.53	0.5	0.21	0.8
3 -2	0.97	14.0	7.7	2.4	1.1	1.8
3 -3	0.98	19.5	5.31	6.2	2.8	3.1
3 -4	0.98	23.6	2.62	16.9	7.7	5.3

[a] Weight fraction of PS in the copolymer component.
[b] Calculated value.

gives the probability of scission per MMA unit. Figure 5 shows x' as a function of Y. For all these samples, $t=10$ min. We see that x' increases with increasing Y, i.e., the higher the concentration of the living ends relative to that of the ester groups is, the more frequent the main-chain scission is. We also see that PMMA and SMAL give nearly the same results. This means that the probability of scission is a function of the concentration of MMA units, but independent of the microstructure of the chain.

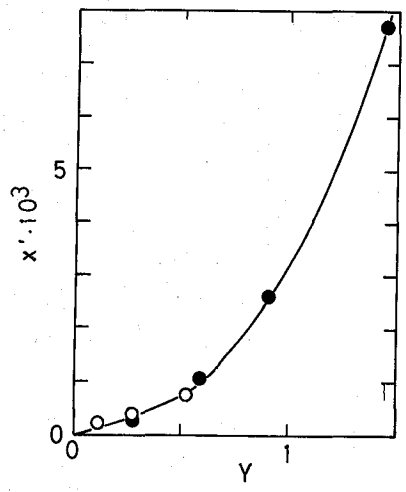

Fig. 5. Plot of x' vs. Y for the samples of series 21 (open circles) and series 3 (filled circles).

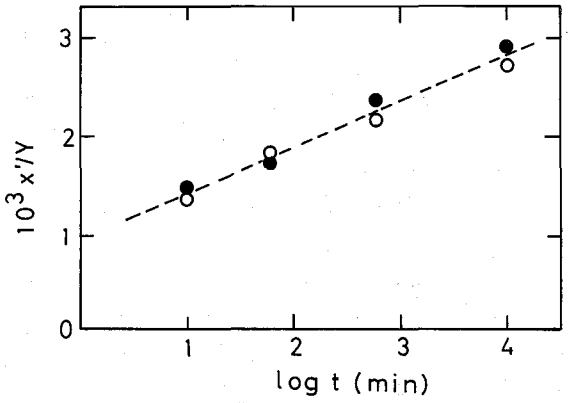

Fig. 6. Plot of x'/Y vs. log t for samples 21–3, 22–1, 22–2 and 22–3 (Y=0.280, open circles) and samples 21–4, 23–1, 23–2 and 23–3 (Y=0.524, filled circles).

From these results, participation of living PS and MMA units in the scission reaction is clear. We also note that x' is approximately proportional to Y when Y is smaller than about 0.6. Along with the result given in Figure 3, it is estimated that under these conditions, a scission reaction occurs once every 750 grafting reactions, a rather small figure. Such a small probability of scission may usually be difficult to detect, insofar as systems with only a small number of grafts per backbone chains are treated, like in previous works[1–3].

In Figure 6, the ratio x'/Y is plotted against reaction time t, showing that x'/Y increases with increasing t and that for the two different values of Y, x'/Y is nearly the same. Thus, x' increases with reaction time and is approximately proportional to Y at all t.

Dimerization of Precursor PS Chains

As already noted, the GPC curves for the components supposedly ascribed to the ungrafted PS were often anomalous (Figures 1c and d). Figure 7 shows the GPC UV-pattern for sample 1–4, for which the anomalies are the most evident. The pattern have two apparent peaks. The lower-elution volume peak (chain-dot curve) is due to the copolymer component, which, because of the many scissions it received ($x=45$), has largely shifted rightwards from the due position, partly overlapping the ungrafted-PS peak. On the other hand, the shape and position of the latter peak are considerably different from those of the precursor PS. As the figure shows, it can be devided into two components, one which is identified with precursor PS (broken curve), and the other of higher molecular weight (dotted curve). Independent GPC runs carried out with standard PS's confimed that the higher-molecular weight component corresponds to the dimerized precursor PS. Thus dimerization of the precursors occurs in this system, and this phenomenon becomes more and more significant as Y becomes larger.

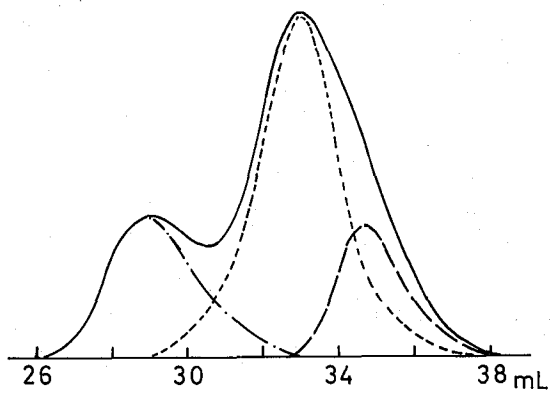

Fig. 7. UV-detected GPC chromatogram for sample 1–4.

Possible Reaction Scheme

We have seen that grafting of living PS onto PMMA is accomanied by the side reactions which result in (1) scission of the main chain and (2) dimerization of the ungrafted PS chains. Both phenomena become more and more significant as Y and/or t increase. We should also note that (3) when Y and t are large, the whole system, orange in color, sometimes gels, and by adding a few drops of methanol, it readily turns to a non-viscous colorless liquid; and that (4) a small amount of solvent-insoluble component is ocassionally found in the product. At present, we have no definitive explanation for all that are happening in this system, but wish to propose a preliminary reaction scheme, as is able to interpret the above observations fairly consistently.

In Figure 8, process (a) is the grafting reaction. That frafting actually occurs is clear, since we have observed increases in molecular weight after the reaction. To obtain more direct, structural evidence for the grafting, we made the following model experiments: A living PS oligomer with a DP of about 10 and PMMA-2 were mixed at a Y ratio of about 0.2. The orange color of the PS anion disappeared shortly after the

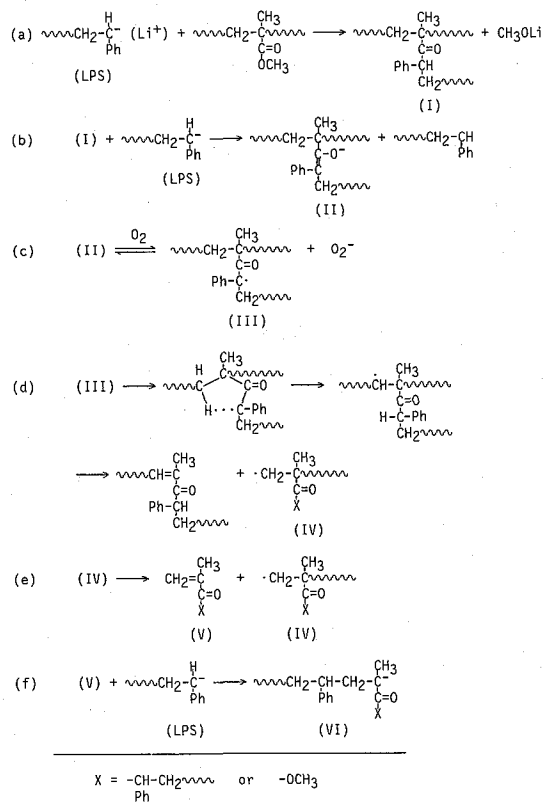

Fig. 8. Postulated reaction scheme for the grafting of living PS onto PMMA or MMA copolymer.

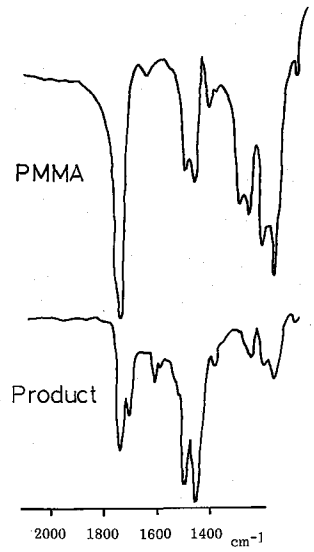

Fig. 9. IR spectra for the precursor PMMA and the reaction product.

mixing, indicating completion of the reaction. Gas chromatographic analysis of the product semi-quantitatively detected methanol derived from lithium mehtoxide. The IR spectrum (Figure 9) shows that the product has a new peak, just by the sharp ester-carbonyl absorbance around 1720 cm^{-1}, due to a ketone-type carbonyl group. These confirm process (a).

Processes (b) through(f) are side reactions: (b) is an enolization reaction, familiar among low-molecular weight compounds. A living PS abstracts the methyne proton of the PS unit linked to the carbonyl carbon to produce a dead PS and a lithium enolate. The presence of a catalytic amount of oxygen is assumed in process (c), which is similar to the known equilibrium process forming an α-keto radical[12]

In process (d), the radical in the side chain is transferred to the main chain, thus causing a bond cleavage. Since the polymer radical IV, in which X denotes either PS or OCH_3,

is unstable, i.e., reactive[13], it can cause another scission on some other chain following the abstraction of its proton or depolymerize according to process (e) producing V, i.e., a monomer (X=OCH_3) or a macromer (X=PS). If this monomer or macromer adds to the living PS remaining in the system, anion VI will result. When X=PS, this macromer is likely to undertake no more addition for a steric reason, and eventually be recovered as a dimer of the PS precursors.

Some more words may be due regarding the present scheme. Firstly, precesses (b) through (d) describe the mechanism of the main-chain scission. According to this scheme, the number of scissions should increase with increasing concentration of living (ungrafted) PS and also with increasing reaction time. This is qualitatively consistent with the experimental results (Cf. Figures 5 abd 6), even though quantitative discussion is presently difficult because of the lack of sufficient data. Secondly, our scheme assumes that the dimerization of PS occurs between a living PS and a macromer having a PS substituent (process (f)). Since this macromer is considered to have been produced by depolymerization of the graft copolymer (process (e)), it follows that a half amount of the PS dimer comes from the copolymer. If this is taken account of, the R_M value of sample 1–4 (GPC curve in Figure 7) should be increased from 0.17 to 0.36, a more reasonable value with regard to other data points (see Figure 2). For the other samples, however, the dimerization is less significant such that the similar correction to their R_M values is less than a few precent in all cases. Thus our scheme is able to interpret the anomalaously low R_M value observed for sample 1–4. Thirdly, anion VI might be a cause for the already-noted gelation of the system, since this type of anions (e.g., MMA anion) are well known to undergo, in a nonpolar solvent like benzene, association among themselves, sometimes gelling the solution. It is also noted that the various types of polymeric radicals appearing in our scheme can recombinate among themselves to produce an insoluble component of very high molcular weight, like the one experimentally observed.

We have shown that the proposed reaction scheme fairly consistently describes the experimental observations. However, since the series of side reactions suggested in our scheme is based on the presence of a catalytic amount of oxygen, experiments carried out in the total absence of oxygen will be required before more definitive conclusion is reached. However, perfect ellimination of oxygen from the system without causing new diffcuties seems at present difficult, and this remains as a future problem.

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